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ELECTROCHEMICAL SYNTHESIS OF FLUOROANHYDRATES OF PERFLUOROCARBONIC AND PERFLUORSULFO ACIDS

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Fluoroanhydrides of perfluorocarbonic acids and sulfo-acids (C7 and more), produced by a method of electrochemical fluorination (ECF), are of great industrial interest. They are raw materials for synthesis of high-performance fluorine surfactants for metallurgy and transport, for manufacture of fluoropolymers etc.[1]. But their synthesis is limited by low yields due to destruction of the initial substrate and resinification during the electrolysis process.

There was carried out a research on the process of fluoroanhydride synthesis in ECF of $H(CF_2\text{-}CF_2)_4CH_2OH$ together with $H(C_2F_4)CH_2OH$ (method [2] used earlier) with addition of tertiary amines. The latter, providing solubility of the substrate in HF and electrolyte electroconductivity, result during the ECF process in formation of perfluorinated amines, which are of a commercial interest. Besides, there was carried out ECF of $C_8H_{17}SO_2F$ and *c*-C_6H_5COCl with addition of tertiary amines and a comparison of the obtained results with the data on ECF with NaF and C_4H_9SH additives was made.

Experimental technique

The experiments were carried out in a Simons' electrolyzer [3].

The current load during the experiments was constant and equal to 15A. The current density in all the cases was also constant and was 0.03 A/cm^2.

A solution of liquid HF, contained 5-15 wt% of organic compound to be fluorinated and 5-15 wt% of tertiary amine, was subjected to electrolysis. The electrolysis was carried out with periodical dozing (1-2 times per hour) of the organic mixture.

During the electrolysis process the crude was periodically poured out after passing a certain amount of electricity (200 A*hour\ liter). At that at every stage the current efficiency of crude was determined, as well as each stage was followed by gas-liquid chromatography analysis of the crude.

Experimental results and their discussion

The comparative data on ECF of $H(C_2F_4)_4CH_2OH$, *c*-C_6H_5COCl and $C_8H_{17}SO_2F$ in the presence of tertiary amines and in their absence are given in the table below.

Electrolytic additive Anode current density, A/cm2

Electrolytic additive	Anode current density, A/cm^2	Electricity passed, (A*hour /L)	Current efficiency crude, %	Crude, main components, wt.%		
ECF $H(C_2F_4)_4CH_2OH$	$F(C_2F_4)_4COF$	C_8F_{18}	$(R_F)_3N$*			
$H(C_2F_4)CH_2OH$	0,02	4371 (2186)	21	35	27	-
C_5H_5N	0,03	1062 (1610)	21	22	23	28*
$(C_2H_5)_3N$	0,03	963 (2139)	34	47	28	5
$(C_3H_5)_3N$	0,03	2640 (4000)	40	39	15	25
ECF *c*-C_6H_5COCl	*c*-$C_6F_{11}COF$	$(R_F)_3N$*				
NaF	0,03	611 (1222)	46	55	-	
C_5H_5N	0,03	246 (546)	57	53	14	
$(C_2H_5)_3N$	0,03	231 (462)	70	-	-	
$(C_3H_5)_3N$	pulsation: 30"-0,03A/cm^2 5" -0,001A/cm^2	2708 (5417)	67	50	25	
ECF $C_8H_{17}SO_2F$	$C_8F_{17}SO_2F$	C_8F_{18}	$(R_F)_3N$*			
NaF,C_4H_9SH [5,6]	=< 0,002	-	up 40	-	-	-
$(C_3H_7)_3N$	0,03	1133 (1718)	46	57	20	12

$(C_3H_5)_3N$	0,03	1584 (2400)	52	50	14	24

** the percentage of the main product of amine fluorination is given here, i.e. its perfluorinated analog; in case of C5H5N it is perfluoropentane C_5F_{12}*

It is seen from the given data that in the presence of $(C_2H_5)_3N$ and $(C_3H_5)_3N$ the current efficiency of the crude of ECF of alcohol-telomer $H(C_2F_4)_4CH_2OH$ is increasing considerably. Resinification of the electrolyte and corrosion of the anodes are decreasing. An additive of n-triallylamine was found the most efficient: the current efficiency of the crude increased almost twice (40%) and duration of continuous operation of the electrolyte increased twice also (up to 4000 A*h/L).

Addition of n-tertiary amines in the electrolyte in ECF of benzoilchloride c-C_6H_5COCl allows increasing the current efficiency of the crude from 46 to 60-70%. The electrolysis of c-C_6H_5COCl in the presence of $(C_3H_5)_3N$ at periodically decreased current density was stable during a long time (over 5000 A*h/L) and the current efficiency of the crude was 67%.

Investigation of combined fluorination of tertiary amines and alkylsulfuryl fluorides was carried out with perfluorooctanesulfuryl fluoride, as an example, which is used for different purposes in industry. One of the fields of its application is its use as a feedstock for manufacture of surfactants .

Methods to produce $C_8F_{17}SO_2F$ using $C_8H_{17}SO_2Cl$ [4] and $C_8H_{17}SO_2F$ [5,6] as the raw for ECF are known.

In the ECF of $C_8H_{17}SO_2Cl$ the electrolysis at 25% yield run for a short time, then the yield is decreased considerably, probably, due to participation of chlorine in the process [4].

In the process of ECF of $C_8H_{17}SO_2F$ it is necessary to use an electrolytic additive, as the solution of octanesulfuryl fluoride in hydrogen fluoride is non-conductive. It is possible to use sodium fluoride [5] or mercaptan (n-butylmercaptan is used most often) [6] as the electrolytic additive. But addition of fluorides of alkali metals results in increasing the rate of corrosion of nickel anodes and does not reduce electrolyte resinification. The main shortcoming of using mercaptans is their strong foul odor and extremely low threshold of sensitivity. This makes difficult their use in industry according to ecostandards.

One of grave disadvantages of the existing methods to produce $C_8H_{17}SO_2F$ is sufficiently quick reduction of current efficiency of the desired product that results on an industrial level in a considerable cost increase.

Our experiments have shown that addition of tertiary amines makes possible decreasing electrolyte resinification during the electrolysis process and increasing the electrolysis duration at a higher current efficiency of the crude. At that in the electrolysis process there are generated by-products which are in demand in industry, namely perfluorinated amines and perfluorocarbons which are unique dielectric liquids, heat carriers, solvents etc..

According to literature data [1,4], the electrochemical synthesis of $C_8H_{17}SO_2F$ is usually carried out at very low current densities (0.001-0.002 A/cm^2) with the purpose to reduce the rate of reactions of destructive fluorination of the initial organic substance. Introduction of additives of tertiary amines makes possible to increase the operating current densities up to 0.03 A/cm^2.

The given above data have shown that the method suggested in this work allows improving the process characteristics for electrochemical synthesis of perfluorinated organic substances of various chemical classes.

At that there are generated by-products in form of perfluorinated tertiary amines which are distinguished by unique thermal physic and dielectric characteristics and find wide application in different engineering areas.

Conclusion

There has been developed an efficient ECF method that allows fluorinating various organic substances, even poorly soluble in HF or forming non-conducting solutions with HF, through the usage of tertiary amines for electrolytic additives.

At that perfluorinated organics belonging to various chemical classes are produced in rather high yield. Those perfluorinated substances are promising surfactants, dielectric heat carriers, materials for chemical current sources.

Cited literature

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